LLNL-JRNL-655538

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June 5, 2014

Meteoritics and Planetary Science

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Abstract - Data obtained from Sm-Nd and Rb-Sr isotopic measurements of lunar highlands samples are renormalized to common standard values and then used to define ages with a common isochron regression algorithm. The reliability of these ages is evaluated using 5 criteria that include whether: (1) the ages are defined by multiple isotopic systems, (2) the data demonstrate limited scatter outside uncertainty, (3) initial isotopic compositions are consistent with the petrogenesis of the samples, (4) the ages are defined by an isotopic system that is resistant to disturbance, and (5) the rare earth element abundances determined by isotope dilution of bulk of mineral fractions match those measured by in situ analyses. From this analysis it is apparent that the oldest highlands rock ages are some of the least reliable, and that there is little support crustal ages older than ~4.40 Ga. A model age for ur-KREEP formation calculated using the most reliable Mg-suite Sm-Nd isotopic systematics, in conjunction with Sm-Nd analyses of KREEP-basalts, is 4389±45 Ma. This age is a good match to the Lu-Hf model age of 4353±37 Ma determined using a subset of this sample suite, the average model age of 4353±25 Ma determined on mare basalts with the ^{146}Sm-^{142}Nd isotopic system, with a peak in Pb-Pb ages observed in lunar zircons of ~4340±20 Ma, and the oldest terrestrial zircon age of 4374±6 Ma. The preponderance of ages between 4.34 and 4.37 Ga reflect either primordial solidification of a lunar magma ocean or a widespread secondary magmatic event on the lunar nearside. The first scenario is not consistent with the oldest ages reported for lunar zircons, whereas the second scenario does not account for concordance between ages of crustal rocks and mantle reservoirs.

INTRODUCTION

Dynamical studies of the origin of the Moon suggest that it formed from the accretion of material ejected from the collision between a Mars-sized body and the early Earth in an event known as the Giant Impact (Hartmann and Davis, 1975; Boss and Peale, 1986). Although this theory is fairly well established, the timing of the impact event remains poorly constrained. The most direct approach to determining the age of the impact event is to measure the age of the oldest rocks present in the Earth-Moon system. Because geologic activity on Earth has destroyed the primary crustal rocks, the search for the most ancient samples has turned to the Moon. However, one of the challenging aspects of determining the age of the Moon through chronologic determinations of the oldest samples is identifying the earliest crustal rocks and distinguishing them from rocks produced by subsequent magmatic events.

A great success of the Apollo program was the development of a relatively simple petrogenetic scenario for the primordial differentiation of the Moon known as the lunar magma ocean model (e.g., Wood, 1970; Smith et al., 1970) that provided such a distinction. In the magma ocean model of lunar differentiation, the Moon accreted after the Giant Impact as a partially (Solomon, 1986) or completely molten body (Binder, 1986; Pritchard and Stevenson, 2000). As the Moon solidified, the initial cumulates were dominated by the relatively dense minerals olivine and pyroxene (e.g., Snyder et al., 1992). Plagioclase cumulates that crystallized later in the differentiation sequence had low Mg/(Mg+Fe), were less dense than their parental magmas, and consequently floated forming the rocks of the ferroan anorthosite (FAN) crustal suite. The last material to form during primordial solidification of the Moon had high abundances of incompatible elements that were not partitioned into the previously formed cumulates. This material is known as ur-KREEP (Warren and Wasson, 1979; Warren et al., 1981) because it has high abundances of potassium (K), rare-earth elements (REE), and phosphorous (P). Magnesium-rich mid- to lower-crustal plutonic rocks with ur-KREEP geochemical signatures, found predominantly at the Apollo 17 site, were thought to represent a later period of Mg-suite magmatism that occurred after the formation of the anorthositic crust and ur-KREEP (Shearer et al., 2006). Thus, the lunar magma ocean model suggested that age determinations of FANs would directly date magma ocean solidification, whereas ages on Mg-suite rocks would provide a minimum age of this differentiation event.

This relatively simple petrologic model for the Moon was developed exclusively from samples collected on the lunar nearside during the Apollo and Luna missions and from remote sensing data collected in the 1970s. Subsequent investigations paint a significantly more complicated picture of lunar differentiation and evolution. For example, although the lunar highlands are dominated by feldspathic rocks, they do not appear to be exclusively ferroan in composition (Ohtake et al., 2012). In fact, studies of lunar meteorites demonstrate that anorthosites with high Mg/(Mg+Fe) are abundance in the lunar surface (Arai et al., 2006; Gross et al., 2014; Joy and Arai, 2013; Korotev, 2005; Korotev et al., 2003, Takeda et al., 2006). Although many of the Mg-anorthosites are recrystallized polymict clastic breccias (granulites), some appear to be primary igneous lithologies. The Mg-anorthosites with igneous textures have been argued to represent more primitive members of the anorthosite rock suite requiring a revision of the classic magma ocean differentiation trend (Takeda et al., 2006). Production of FANs by partial melting of plagioclase-rich cumulates has even been suggested (Longhi, 2003), implying that FANs may not necessarily represent primordial crust formed during solidification of a magma ocean. Likewise, magnesium-rich plutonic rocks, once thought be ubiquitous in the crust, are largely absent in meteorites samples and not widespread on the surface (Jolliff et al., 2000; Korotev, 2005; Korotev et al., 2003, 2009; Wieczorek and Phillips, 2000; Wieczorek et al., 2006) making it difficult to evaluate whether they represent widespread plutonic magmatism that was initiated after magma ocean solidification or were associated with limited magmatic activity exclusively on the lunar nearside.

Chronologic investigations have not clarified the petrogenisis of the FANs and Mg-suite, but instead have served to confirm the geologic complexity of the lunar crust. Ages determined on FANs range from 4.29 to 4.57 Ga implying that either the lunar magma ocean cooled over an extended duration of ~300 Ma, or that not all FANs are cumulates of the magma ocean (Borg et al., 1999). Several FANs are younger than ages reported for some Mg-suite rocks (Figure 1) consistent with formation of FANs outside the context of the magma ocean (Shih et al., 1993; Borg et al., 1999). In fact, some of the oldest ages determined on lunar rocks are from samples of the Mg-suite which are not considered to be primordial magma ocean products (Shearer et al., 2005). Thus, the ages determined on lunar crustal rocks provide little support for the classic lunar magma ocean model of lunar differentiation, and clearly cannot be used to directly constrain the age of the Moon. However, it is important to note that age determinations of the oldest lunar samples have proven to be extremely challenging because all terrestrial bodies, including the Moon, experienced significant meteorite bombardment after their formation that destroyed many of the oldest surface samples and disturbed the isotopic systematics of the remaining material. Therefore, the apparent large range of FAN ages, as well as apparent overlap between ages of FANs and Mg-suite rocks, could simply arise from the inability to accurately determine ages on ancient rocks that have experienced complex, and often intense, post crystallization metamorphic histories.

Reanalyzing all of the lunar samples for which ages have been obtained over the last 40 years using modern state-of-the art-techniques is not feasible because of the amount of labor involved as well as the limited availability of many of these samples. Furthermore, there is no *a priori* reason to expect more modern age determinations to always be more accurate than the ages determined previously given the heterogeneous nature of isotopic disturbances in lunar samples. The goal of this investigation, therefore, is to better constrain the temporal relationships of crustal rocks by identifying the most reliable crystallization ages. In this context, the crystallization ages are compared to model ages of lunar differentiation, as well as to ages determined from "detrital" zircons found in lunar breccias in order to determine if a common age for lunar crust formation and differentiation can be derived from the published literature.

ISOCHRON AGES OF HIGHLANDS SAMPLES

The most common isotopic systems used to date the crystallization of highlands rocks are Rb-Sr, Sm-Nd, and Pb-Pb. Chronologic investigations in the first decade after the Apollo missions also utilized U-Pb concordia diagrams to obtain crystallization ages. However, this method has become less common in recent chronologic studies as a result of the complex disturbances to U-Pb isotope systematics in lunar rocks. Chronologic investigations of highlands rocks that were undertaken soon after the first samples were returned from the Moon commonly showed that their isotopic systematics were disturbed. These disturbances were evident when isotopic data were plotted on isochron diagrams, and individual mineral or whole rock fractions from single samples showed greater scatter about a best-fit isochron than can be attributed solely to analytical uncertainty. It also became apparent that ages produced on the same rocks in different laboratories, or using different isotopic systems, did not agree (e.g., Papanastassiou and Wasserburg, 1976; Lugmair et al., 1976). Specific factors that are likely to be responsible for these observations include: (1) disturbance of the isotopic systematics of lunar samples by secondary processes associated with impacts, (2) the difficulty associated with dating mono- or bi-mineralic samples that have low abundances of the parent and daughter isotopes, and (3) inter-laboratory differences in standardization, measurement techniques, and age calculations. In the following sections, mechanisms that disturb the isotopic systematics of lunar samples are examined and criteria are developed that allow the most reliable ages to be identified.

Isotopic disturbance by impact metamorphism

Isotopic disturbances in lunar highlands samples have been well documented, and for the most part, have been attributed to late bombardment of the lunar surface resulting in widespread thermal metamorphism of the crust (Tera et al., 1974; Nyquist, 1977). Impact metamorphism was most intense in early lunar history prior to ~3.8 Ga (e.g. Nyquist and Shih, 1992), and consequently is a significant impediment to obtaining ages on the oldest crustal rocks from the highlands. Impact processes can disturb isotopic systematics by heating the samples and causing redistribution of parent and daughter isotopes, as well as by introducing foreign contaminants in the form of minerals, rock fragments, or impact melts.

Understanding the effects of impact metamorphism is complicated by the fact that each isotopic system responds differently to secondary disturbances based on the chemical behavior of the parent and daughter elements, and their distribution in the sample and contaminant. For example, one isotopic system may be completely reset by thermal metamorphism, and therefore record the age of the metamorphic event, whereas another chronometer applied to the same minerals may be completely unaffected by metamorphism and instead record a crystallization age. The diffusion of Rb, Sr, U, Pb, Sm, and Nd in silicate minerals under typical conditions of thermal metamorphism associated with impacts is slow enough that fully resetting these systems in the absence of complete melting is unlikely. Instead, thermal metamorphism tends to disturb the isotopic systematics of samples resulting in scatter on isochron diagrams (e.g., Borg et al., 1999; Gaffney et al., 2011). Experimental investigations of shocked and heated lunar samples demonstrate that the Sm-Nd chronometer is the least affected during metamorphism and is therefore the most reliable recorder of igneous events in samples that experienced post-crystallization heating (Gaffney et al., 2011). As a consequence, this chronometer is most commonly used to determine the ages of highlands samples. In contrast, the Rb-Sr and U-Pb isotopic systems are more easily disturbed. This stems, in part, from the greater volatility, and hence mobility, of Rb and Pb compared to Sr, U, and REE during heating. As a result, Rb-Sr and U-Pb crystallization ages are often obtained by including only those mineral and whole rock fractions in the isochron regression that are thought to have remained undisturbed. This is a subjective process, however, and can lead to derivation of significantly different ages from the same data sets (e.g. Premo and Tatsumoto, 1992; Borg et al., 1999; Hana and Tilton, 1987; Borg et al., 2011).

Contamination of mineral separates used to define isochrons by extraneous minerals can affect isotopic age determinations of clast samples separated from matrix material. Samples from the Moon are particularly susceptible to this type of disturbance because the Moon is a relatively small water-poor body, and consequently crystallizes only a limited number of phases. As a result, isochron systematics are often dominated by the abundances of a single phase in the mineral fractions, such as plagioclase in the Rb-Sr system, or phosphate in the Sm-Nd system. Addition of small amounts of extraneous minerals to individual mineral fractions will cause systematic shifts in their isotopic compositions that result in erroneous age determinations. In fact, such linear mixing arrays on isochron diagrams are predicted if a single phase containing a high abundance of the daughter isotopes is distributed proportionally into the various mineral fractions (Shearer et al., 2012). The problem is exacerbated by the fact that the extraneous mineral phases usually have mineralogical characteristics that are similar to the indigenous minerals, and are therefore very difficult to detect. The clearest manifestation of such mixing lines are initial isotopic compositions derived from the isochrons that are not consistent with the petrogenesis inferred for the sample from mineral and whole rock chemistry (Shearer et al., 2012).

Inter-laboratory analytical differences

Although the Sm-Nd isotopic system is the most difficult to disturb by metamorphic processes (Gaffney et al., 2011), replicate Sm-Nd measurements completed by different laboratories on the same samples are often discordant. For example, ranges of Sm-Nd ages determined on troctolite 76535 are 4.25 to 4.44 Ga (Lugmair et al., 1976; Premo and Tatsumoto, 1992; Nyquist et al., 2012), on norite 78236/8 are 4.33 to 4.44 Ga (Carlson and Lugmair, 1981a; Nyquist et al., 1981; 2008; Edmunson et al., 2009) and FAN 60025 are 4.36 to 4.44 Ga (Carlson and Lugmair, 1988; Borg et al., 2011). The Sm-Nd ages reported on these rocks differ outside the reported analytical uncertainty, underscoring the inability of error calculations to define the accuracy of individual ages. This is because age uncertainties are based on the degree to which individual data points lie near the regressed isochron. An uncertainty calculated in this manner is a good reflection of disturbance of the isotopic systematics by metamorphic events or analytical issues associated with single analyses (i.e. poor isotope ratio measurement). However, differences in ages reported for single samples by individual laboratories are most likely due to factors other than disturbance of the isochron by metamorphism. Other factors include: (1) variable purity of the mineral fractions, (2) differences in spike calibration, (3) magnitude of laboratory induced contamination (blank), (4) the magnitude of interfering element corrections associated with mass spectrometry measurements, (5) measurement bias indicated by disparate values obtained for isotopic standards, and (6) use of different algorithms to calculate ages from isotopic measurements. Evaluating the contribution that these factors have on the reported ages is not possible in hindsight. However, isotope ratio measurements can be corrected to common isotopic standard values and ages can be calculated using a common algorithm.

RELIABILITY OF ISOCHRON AGES

Evaluation of highlands sample ages

The first step in evaluating the reliability of published isochron ages of highlands rocks is to minimize the effects of inter-laboratory analytical bias. To accomplish this published lunar isotopic data are normalized to common standard values (NBS-987 $^{86}Sr/^{86}Sr$ = 0.710245; LaJolla $^{143}Nd/^{144}Nd$ = 0.511845). Ages are then calculated using a single regression algorithm (IsoPlot 4.15), to remove inter-laboratory biases associated with different isochron calculation methods. Mineral fractions preferred by the authors of each study are used as the basis for the age calculations. Uncertainty on the ages is calculated using 2 times standard deviations of repeat isotope ratio measurements on standards or 2 times the standard errors reported for the ratio measurements, whichever is higher. Ages are calculated for FANs and Mg-suite rocks using data reported in chronologic investigations and are presented in Table 1.

Criteria to establish reliability of isochron

The ages presented in Table 1 are evaluated using a common set of criteria that estimate the probability that the ages record the time of crystallization. The five criteria are discussed below and applied to the published ages in a pass/fail mode. The first criterion (1) is whether concordant ages have been determined using multiple chronometers. Two or more concordant ages derived from the same mineral separates using multiple chronometers provides the strongest indication that the measured isotopic systematics record the crystallization age of the sample (e.g., Borg et al., 1997). Unfortunately, few highland samples have yielded such concordant ages either because multiple systems were not applied, or because metamorphism has disturbed some isotopic systems. Additional criteria are therefore necessary to evaluate ages determined using a single isotopic system. There are four additional criteria that are used below to evaluate the reliability of published crystallization ages. They include: (2) linearity of individual isochrons, (3) resistance of the isotopic system to disruption by impact heating or contamination, (4) consistency between measured initial isotopic compositions and the inferred petrogenesis of the sample, and (5) reasonableness of parent and daughter elemental concentrations of the mineral fractions.

An age reliability index is calculated based on the number of criteria the data obtained in an individual age investigation meet. This index helps to define the relative reliability of an age determination in the context of other highlands rock ages. This index is not intended to be used to demonstrate that a particular age is incorrect, or that a particular set of ages defines a specific episode of lunar magmatism. Instead, this index should be used to evaluate how reliable an individual age measurement is likely to be relative to other ages reported in literature. The reliability index may be particularly useful in cases where multiple age determinations have been made on single samples.

Isochrons ages defined by a large number of large mineral fractions are preferable to ages based on a few mineral fractions. This stems from the fact that ages defined by multiple mineral fractions are not as strongly dependent on a potentially erroneous measurement completed on a single mineral fraction. Despite this benefit, the number of mineral fractions used to obtain an age is not one of the criteria used to evaluate reliability. This is because the amount of lunar material available for chronologic investigations is limited so that mineral fractions must be small if numerous fractions are produced from a single sample. Smaller mineral fractions are more susceptible to laboratory contamination, as well as increased analytical uncertainty resulting from smaller ion beam intensities. For Sm-Nd analyses completed on lunar samples, the smallest fractions are 1-2 ng in size and require Nd to be run as an oxide on a thermal ionization mass spectrometer. Neodymium oxide measurements are further susceptible to errors associated with interfering element corrections, such as $^{141}Pr^{18}O$ on $^{143}Nd^{16}O$ and $^{142}Ce^{18}O$ on $^{144}Nd^{16}O$, as well as mass fractionation of oxygen in the instrument. In contrast, large mineral fractions are usually run as Nd^{+} metals for long durations on mass spectrometers yielding significantly more precise and reproducible isotope ratio measurements than can be obtained from the analysis of smaller fractions. Thus, there are pros and cons of analyzing numerous small mineral fractions versus a few large mineral fractions. Because it is not clear how the reliability of an individual age is related to the number of fractions analyzed, this criteria is not used in this evaluation.

Criterion 1 – Age determined by multiple chronometers

Samples that yield concordant ages from multiple isotopic systems almost certainly record a crystallization event, whereas ages determined by single chronometers should be considered more cautiously. Isotopic disturbances associated with metamorphism or with analytical issues appear to be minimal in cases where concordant ages are determined with multiple chronometers (Edmunson et al., 2009; Borg et al., 1997; 2011). Furthermore, contamination processes that produce linear arrays on isochron diagrams are unlikely to yield concordant ages from multiple isotopic systems. Thus, ages determined using multiple chronometers pass this criterion.

Criterion 2 – Limited scatter on isochron plots

Isochron ages are calculated from the slopes of regressions fit through data points using formulations originally presented by York (1966) or Williamson (1968). Linearity of the fractions on the isochron is the basis for calculating the age uncertainty and is traditionally the main criteria by which the reliability of the age is evaluated. Although this uncertainty does not strictly reflect the accuracy of the age determination (see above), it provides a basis to assess the mobility of parent and daughter isotopes during metamorphism, as well as the ability of individual laboratories to make self-consistent isotopic measurements. The degree of linearity of the regressed data is evaluated using both the uncertainty associated with the age calculation and the mean square weighted deviation (MSWD) of the regression. The MSWD reflects the degree to which individual data points fit the calculated regression of the data, taking into account the analytical uncertainties associated with the data. A good fit of the data to the regression is reflected by MSWDs of ~1, whereas values higher than ~5 are usually deemed to indicate a poor fit. Very low MSWD are also problematic but suggest an underestimation of analytical uncertainty and do not necessarily imply an incorrect age is defined by the isochron. In the evaluation of ages presented below, an uncertainty < 85 Ma, or a MSWD < 5 are considered to be evidence that an age is likely to be reliable.

Criterion 3 – Chronometer resists disturbance by thermal metamorphism

The third criterion that is used to assess reliability of ages is the resistance of the chronometers used to obtain the age to resetting by heating associated with impact metamorphism and to contamination. Isotopic systems such as Ar-Ar, Rb-Sr, Pb-Pb, and U-Pb are more easily disturbed than the Sm-Nd isotopic systems and are consequently less likely to represent crystallization ages (e.g., Borg et al., 1999; Gaffney et al., 2011). Therefore, it is reasonable to put more credence in Sm-Nd crystallization ages than on Rb-Sr ages for example. Although U-Pb and Pb-Pb can record crystallization events in impact metamorphosed samples (Edmunson et al., 2009; Borg et al., 2011), mobility of Pb during heating events and contamination by Pb in the sample makes this system less reliable than Sm-Nd. Thus, ages determined by Sm-Nd meet this criterion, whereas those determined by Rb-Sr, Pb-Pb, and U-Pb do not. It is important to note, however, that the strongest support for a correct Sm-Nd age are concordant ages determined by other isotopic systems, even those systems that are deemed to be more easily reset by post crystallization processes.

Criterion 4 – Initial isotopic compositions are consistent with petrogenesis

The fourth criterion is the consistency between the initial isotopic composition of the rock and its inferred petrogenesis. Initial Nd isotopic compositions determined on several FANs and Mg-suite rocks are strongly positive (+1 to +3 epsilon units) , indicating that these rocks are derived from LREE-depleted source regions (Carlson and Lugmair, 1988; Shih et al., 1993; Borg et al., 1999). Trace element abundances in mineral phases, however, suggest these rocks are derived from moderately to highly LREE-enriched sources (Papike et al., 1994; 1997; Floss et al., 1998). Such inconsistencies probably reflect either analytical issues, such as inappropriate spike calibrations or interfering element corrections, or physical mixing of contaminants into the dated samples.

In order for a highlands sample to meet this criterion, the initial Nd and/or Sr isotopic compositions derived from isochrons must fit the modeled isotopic compositions of their postulated sources. The composition of the sources is based on compositional constraints derived from lunar petrogenisis investigations by Snyder et al. (1992) and Warren (1988). Because the incompatible-trace element systematics of FANs indicate that they are derived from chondritic or slightly LREE-enriched source regions an initial εNd value of 0 is considered appropriate for the FAN source (Snyder et al., 1992). The Mg-suite rocks are derived from a LREE-enriched source similar to ur-KREEP (Warren and Wasson, 1979), so that a two-stage growth history is modeled for the Mg-suite source. Isotopic growth in stage 1 occurs in a chondritic reservoir with $^{147}Sm/^{144}Nd$ = 0.1967 until 4.39 Ga. This is the average age of ur-KREEP formation calculated by Carlson and Lugmair (1979) and Nyquist and Shih (1992). Stage 1 is followed by growth in a reservoir similar to ur-KREEP, with $^{147}Sm/^{144}Nd$ = 0.179 (Warren and Wasson, 1979; Warren, 1988) until the present. Strontium isotopic evolution in the Mg-suite source is also modeled in two stages in which the bulk Moon reservoir has $^{87}Rb/^{86}Sr$ = 0.016 (Ganapathy and Anders, 1974; Borg et al., 1999), and the second reservoir has a $^{87}Rb/^{86}Sr$ = 0.29 that is similar to ur-KRREP. Isochrons that yield ages and initial isotopic compositions that are within 1.5 times analytical uncertainty of these growth models meet this criterion.

Criterion 5 – Elemental abundances in mineral fractions match in situ measurements

The final criterion used to assess isochron age reliability is the whether the abundances of parent and daughter isotopes measured in mineral fractions by isotope dilution analysis are consistent with measurements determined by ion microprobe on similar rocks. Unfortunately, in situ ion microprobe concentrations of Rb and Sr have not been systematically measured for all relevant types of highlands samples for which Rb-Sr isochron ages have been produced. Thus, this criterion only applies to Sm-Nd analyses. In addition, mafic mineral fractions are difficult to purify because olivine, orthopyroxene, and clinopyroxene have similar magnetic properties, densities, and appearances under the binocular picking microscope. In contrast, plagioclase is fairly easy to purify using these techniques. Furthermore all Sm-Nd isochrons of lunar highlands samples incorporate at least one plagioclase fraction so that disturbance of the REE systematics of this fraction provides a clear indication that the Sm-Nd isochron regressed through plagioclase could be disturbed. In the test for this criterion, Sm and Nd abundances in plagioclase mineral fractions are compared to SIMS data determined on typical FANs, Mg-suite norites, and

Mg-suite troctolites. Average Sm and Nd abundances reported on FANs (n=22) are 0.067±0.025 ppm and 0.27±0.12 ppm (Papike et al., 1997; Floss et al., 1998; uncertainties are 1 standard deviation of the reported data). The average Sm and Nd abundances reported on norites (n=15) are 1.17±0.32 ppm and 5.38±1.8 ppm, whereas average Sm and Nd for the troctolites (N=20) are 1.81±0.51 ppm and 7.34±1.6 ppm (Papike et al., 1996; Shervais and McGee, 1998). Isochrons defined by plagioclase mineral separates that have Sm and Nd abundances that are within a factor of two of the average values determined by ion microprobe meet this criterion.

RESULTS OF EVALUATION

Table 1 presents the results of this evaluation and includes the recalculated ages, the recalculated initial isotopic compositions, and MSWDs from the isochrons, as well as the concentrations of Sm and Nd measured in the plagioclase mineral fractions. Isotopic studies involving only U-Pb or Pb-Pb are not included in this analysis because of the subjectivity associated with the selection of points used to define the isochrons. These data are included only when they are accompanied by Sm-Nd or Rb-Sr data on the same mineral fractions. In cases where multiple chronometers yield concordant ages, the preferred age of the sample is defined by the weighted average of all concordant ages (bold text in the Table 1). The number of criteria met, referred to as the reliability index, determined for each age investigation is listed in the last column of Table 1. Those criteria that are not met are identified by italics. It is important to keep in mind that a low reliability index determined from this evaluation does not necessarily indicate that an individual age is incorrect. Instead, the reliability index should be thought to reflect the relative probability that an age is correct. Thus, those ages with reliability indices greater than 4/5 have a higher probability of being correct than ages with reliability indices of 2/5.

This evaluation demonstrates that only 4 of the 24 studies evaluated in Table 1 meet 5/5 of the reliability criteria. These include investigations of samples 60025 (4360±3 Ma), 78236/8 (4349±19 Ma), 76535 (4306±10 Ma), and 77215 (4386±22 Ma).

Not surprisingly these are some of the most recently determined ages on the largest igneous samples collected during the Apollo missions. The high reliability indices associated with these measurements reflect the development and application of analytical protocols that define ages using multiple chronometers, the use of modern analytical instrumentation, the availability and selection of relatively large samples, and the absence of significant terrestrial contamination that is sometimes present in meteorite samples (Borg et al., 2009). Five of the 24 studies evaluated in Table 1 meet 4/5 of the criteria including investigations completed on samples 60025 (4437±39 Ma), 78236/8 (4436±51 Ma), 76535 (4330±64 Ma), 77215 (4369±16 Ma), and 67667 (4176±61 Ma). Note that four of these samples have been analyzed in multiple investigations and that the reported ages sometimes differ outside analytical uncertainty. The ages with the highest reliability index are taken to have the highest probability of representing the true crystallization age of the rock (Table 1). In all cases the older ages have been supplanted by younger ages with higher reliability indices. Some ages with reliability indices of 4/5 are concordant with more recently published measurements with higher reliability indices (e.g., 76565). This indicates that the probability that an age with a reliability index of 4/5 would be reproduced by a future investigation having a higher reliability index of 5/5 is roughly even.

The age evaluation presented in Table 1 demonstrates that the oldest ages have some of the lowest reliability indices (Figure 2). There are no samples with ages older than 4.40 Ga that have reliability indices of 4/5 or greater that have not been reanalyzed to yield younger ages with high higher reliability indices. Several samples with ages older than 4.40 Ga, including FANs Y86032 (4438±34 Ma), 67215 (4408±140 Ma), and 67016 (4573±160 Ma) and Mg-suite rocks 76535 (4566±60), 15445 ,17 (4470±70 Ma), 15455 ,228 (4545±150 Ma), and 74217 (4528±92 Ma) have reliability indices of 3/5 or lower. These ages are less likely to record crystallization of the samples than ages with reliability indices of 4/5 or higher. Thus, this evaluation provides only limited support for crystallization ages of the FAN and Mg-suites that are older than ~4.40 Ga.

COMPARISON OF LUNAR CRUSTAL AND MANTLE RESERVOIR AGES

Model ages

Model ages for magma ocean solidification and mare basalt source formation have both been used to constrain the age of the Moon. Several investigations have attempted to determine the age of ur-KREEP formation in order to date when the last lunar magma ocean products solidified. Ur-KREEP Sm-Nd model ages were calculated by Carlson and Lungair (1979) and Nyquist and Shih (1992) to be 4.36±0.06 Ga and 4.42±0.07 Ga, respectively. The Sm-Nd model ages were calculated using all available Sm-Nd age data with little consideration for the reliability of the individual isochron measurements. Recently model ages of ur-KREEP formation of 4402±23 Ma and 4478±92 Ma were calculated by Sprung et al., (2013) and Taylor et al., (2009) from Lu-Hf systematics determined on breccias enriched in K, REE, and P and from zircons assuming a $^{176}Lu/^{177}Hf$ ratio for ur-KREEP. More refined models ages can potentially be obtained using Sm-Nd data selected to meet a high percentage of the reliability criteria, and Lu-Hf data obtained on igneous samples with well defined ages and evolutionary histories.

A Sm-Nd model age for ur-KREEP is presented in Figure 3. It is calculated using the Sm-Nd isotopic compositions of Mg-and alkali-suite samples enriched in K, REE, and P in conjunction with Sm-Nd data obtained on three KREEP-basalts (Gaffney and Borg, 2013; in press). All data used in this calculation meet 4/5 or greater of the reliability criteria discussed above. For samples that have been analyzed in multiple studies (samples 78238, 76535, and 77215), the preferred ages and initial isotopic compositions in Table 1 are used. The model age is defined, following the approach outlined in Edmunson et al., (2009), by the intersection of the line regressed through the data with the growth curve for a chondritic reservoir calculated assuming $^{147}Sm/^{144}Nd$ = 0.1967 and $^{143}Nd/^{144}Nd$ = 0.512638 (Jacobsen and Wasserburg, 1980). The intercept is calculated using IsoPlot 4.15 and defines an age of ur-KREEP formation of 4389±45 Ma (MSWD = 1.8).

Using the same approach Gaffney and Borg (2013; in press) derived a Lu-Hf model age of 4353±37 Ma (MSWD = 0.18) for a subset of the KREEP-rich igneous samples used to determine the Sm-Nd model age. In this case, initial Hf isotopic compositions were calculated using whole rock Lu-Hf isotopic measurements and the most reliable Sm-Nd isochron ages in Table 1. This age is in good agreement with the Lu-Hf model ages determined on breccia samples by Sprung et al. (2013) and Taylor et al (2009), but more accurately reflects an igneous differentiation event because it is based on the analysis of igneous rock samples with comparatively simple geologic histories, well defined crystallization ages, and does not require the ^{176}Lu/^{177}Hf ratio for urKREEP to be assumed. The 4353±37 Ma model Lu-Hf age is concordant with the Sm-Nd model age for ur-KREEP formation of 4389±45 Ma indicating that these models are likely to record a geologic event. The weighted average of the two model ages is 4368±29 Ma and is taken as the best estimate for the formation age of ur-KREEP.

The age of last equilibration of the mare basalt source has been estimated using the ^{146}Sm-^{142}Nd isotopic system. The model age is calculated from the slope of a line regressed through whole rock data on a ^{147}Sm/^{144}Nd-^{142}Nd/^{144}Nd whole rock isochron plot. To calculate a ^{142}Nd model age, the ^{147}Sm/^{144}Nd ratio of the mare basalt sources is plotted against the ^{142}Nd/^{144}Nd to obtain the initial ^{146}Sm/^{144}Sm of the basalt source regions at the time of formation. The ^{147}Sm/^{144}Nd of the source is calculated from whole rock ^{143}Nd/^{144}Nd ratios assuming three stages of isotopic growth (Nyquist et al., 1995). Note that ages calculated in this manner are not dependent on the assumed initial ^{142}Nd/^{144}Nd of the Moon. Implicit in these models is the assumption that isotopic variation observed in the mare basalt source regions reflects fractionation of Sm from Nd from a common source. In the context of a magma ocean model, this represents the fractionation of Sm from Nd during the formation of the mare basalt cumulates. The age recorded in the mare basalts could also record prolonged solidification of late stage magma-ocean cumulates or later re-equilibration of the source regions after their initial formation (McLeod et al., 2014). Ages of 4329 $^{+40}/_{-56}$ Ma (Nyquist et al., 1995), 4352 $^{+21}/_{-23}$ Ma (Rankenburg et al., 2006), 4313 $^{+25}/_{-30}$ Ma (Boyet and Carlson, 2007), 4340 $^{+20}/_{-24}$ Ma (Brandon et al., 2009), and 4355 $^{+31}/_{-39}$ Ma (Gaffney and Borg, 2014) have been determined using this approach. Ages ranging from 4.34±0.02 Ga to 4.39±0.02 Ga have also been calculated for some Apollo 12 basalts assuming various ^{142}Nd/^{144}Nd ratios for the bulk Moon (McLeod et al., 2014). These studies yield a weighted average age of

4353±25 Ma for mare basalt source formation that is in good agreement with the average urKREEP model age of 4368±29 Ma.

Zircon ages

Lead-lead ages have been determined by in situ ion microprobe analysis of zircons found in both igneous samples and in breccias. Although the origin of zircons present in the breccias is unknown, the abundance of this mineral in granites, granophyres, and quartz monzo-diorites suggests that the majority of these zircons are derived from the alkali magmas associated with the Mg-suite. The large number of ages obtained using this method, relative to the number of ages determined from mineral isochrons on large igneous samples, provides a broader picture of igneous crustal evolution. Figure 4 is a histogram of published zircon ages. The ages have been binned into 10 Ma intervals, so that this plot is a representation of ~400 individual spot analyses from 19 different rocks. Although the majority of zircons are from the Apollo 14 and 17 landing sites, a few ages have been obtained from zircons from Apollo 12 and 15 landing sites. As a result, the age distribution is likely to be a reasonable representation of zircon ages from the lunar nearside. Note, however, that some bias is introduced into the oldest age bins as a result of numerous, repeat, analyses of single zircon grains in the search for the oldest ages. For example, a single zircon from breccia 72215 was analyzed 41 times, and accounts for most, but not all, of the ages older than 4375 Ma on Figure 4.

Figure 4 demonstrates that there is a peak of zircon ages at ~4340 Ma. A detailed analysis of 123 zircon ages from sample 14311 and other unspecified Apollo 14 breccias confirms this distribution pattern (Merle et al., 2013). A compilation of reported ion microprobe zircon ages from individual breccia samples is presented in Figure 5. Ages determined from single samples demonstrate substantial ranges. The simplest interpretation is that this range records an extended period of Mg- and alkali magmatism from ~3.8 to 4.4 Ga. Although this interpretation is consistent with large differences in ages of the youngest zircons in each sample, the observation that the youngest ages at many sites are ~3.8 to 3.9 Ga suggests a partial resetting of the ages by the late heavy bombardment. Complex age distributions observed in several individual zircons seem to support this conclusion. Thus, the significance of the youngest zircon ages is not clear. In any case, they probably should not be used to constrain the termination of Mg- suite and alkali magmatism in the absence of detailed analysis of the metamorphic history of individual zircon grains.

The oldest zircon spot ages were measured in samples 14304 (4416±35 Ma), 14321 (4404±20 Ma), 15405 (4429±55 Ma), 73235 (4409±13 Ma), and 72215 (4417±6) by Meyer et al. (1996), Grange et al. (2009; 2011), Nemchin et al. (2008; 2009a) and Taylor et al. (2009) and are concordant (Figure 6). The oldest zircon ages are older than almost all of the other seemingly reliable lunar ages, including the model age for the formation of the mare basalt source regions, and the isochron ages determined on the highland rock suites (Figure 6). Significantly, most are just within analytical uncertainty of the ur-KREEP model age determined from Sm-Nd and Lu-Hf isotopic analyses of the Mg-suite rocks and KREEP basalts. The only zircon age that is discordant from the ur-KREEP model age is from breccia 72215 (Figure 6). This zircon age is not consistent with their inferred petrogenisis, because zircons are thought to be derived from alkali-rich magmas associated with the Mg-suite and ur-KREEP (Snyder et al., 1995). Thus, it is not clear how a zircon could be older than ur-KREEP. If the ages are taken at face value, it seems likely that either the ur-KREEP model age is not recording ur-KREEP formation or the zircon Pb-Pb age is incorrect. On the other hand, perhaps this simply reflects an underestimation of analytical uncertainties. The ur-KREEP model age presented here is only 14 Ma younger than the age reported for the zircon in 72215 by Nemchin et al. (2009a).

RAMIFICATIONS

Evaluation of the existing chronology of lunar samples demonstrates that there is little evidence for the presence of truly ancient samples on the Moon. The apparent absence of ancient lunar samples is consistent with the limited evidence for live short-lived nuclides in lunar samples. Isotopic variations resulting from decay of ^{182}Hf to ^{182}W ($t_{1/2}$= 9 Ma) are very small or absent (Kleine et al., 2005; Kleine et al., 2014), and variation in ε^{142}Nd in lunar samples is very small compared to other solar system bodies, such as Mars (Harper et al., 1995; Borg et al., 1997, 2003; Foley et al., 2005; Debaille et al., 2007; Caro et al., 2008), the eurcite parent body (Wadhwa and Lugmair, 1996), or the angrite parent body (Lugmair and Galer, 1992; Nyquist et al., 1994). Instead there appears to be a preponderance of ages recorded on the Moon and on Earth between 4.34 and 4.37 Ga (Figure 7). These include the average ur-KREEP model age (4368±29 Ma), the average mare basalt model age (4353±25 Ma), the most reliably dated FAN 60025 (4360±3 Ma), the oldest most reliably dated Mg-suite rock 78236/8 (4349±19 Ma), the peak in lunar zircon ages (4340±20 Ma) and the average spot age of the oldest terrestrial zircon 01JH36-69 (4374±6; Valley et al., 2014). All of these ages are within uncertainty of one another, with the exception of the terrestrial zircon and the FAN 60025 age which differ by 5 Ma. Thus, there appears to be a convergence between the ages of the oldest reliably dated lunar crustal rocks, the age of the oldest terrestrial sample, the age of lunar mantle isotopic equilibrium, and the apparent formation age of ur-KREEP at 4.34 to 4.37 Ga (Figure 7). The most notable age that does not fit into this age spectrum is the 4417±6 Ma age determined on the 72215 zircon (Figure 6) by Nemchin et al. (2009a).

There are two scenarios that can account for the 4.34 to 4.37 Ga spectrum of ages observed on the Moon. The first is mostly consistent with classic petrogenetic models for the differentiation of the Moon that are based on the concept of a global magma ocean (e.g., Snyder et al., 1992). The second scenario requires the Moon to have a more complicated petrogenetic history. These two scenarios are discussed below.

The simplest explanation for the preponderance of ages between 4.34 to 4.37 Ga is that they reflect the time when a lunar magma ocean passed below the closure temperature of the various chronometers. In this scenario, ur-KREEP, the mare basalt source regions, and FANs are considered to be primordial solidification products of the lunar magma ocean. Thus, the average age of ur-KREEP formation, mare basalt source region equilibration, and crystallization of FAN 60025 of 4355±32 Ma is likely to be the best representation of the age of primordial solidification of the Moon through the blocking temperature of the Sm-Nd system. In order for this scenario to be correct, Mg-suite magmatism must be essentially contemporaneous with solidification of the magma ocean and the formation of ur-KREEP, mafic mantle cumulates, and anorthositic crustal cumulates. It also requires the oldest ages determined on lunar crustal samples, as well as oldest age determined on lunar zircon 72215, to be in error.

An alternative scenario is that the 4.34 to 4.37 Ga event recorded in the lunar crustal samples represents a period of widespread Mg-suite and FAN magmatism on the lunar nearside that followed an earlier planetary scale differentiation event. One advantage of this scenario is that it provides a mechanism for producing both FAN and Mg-suite lithologies contemporaneously. Another advantage of this scenario is that the zircon age from breccia 72215 of 4417±6 Ma is not problematic, and simply provides the oldest reliable age for lunar crustal formation. In this second scenario, ur-KREEP, the mare basalt source regions, and FANs cannot be considered to be primordial solidification products of the lunar magma ocean, and instead must have experienced a more complicated and extended thermal history. Ferroan anorthosite 60025 would represent a magmatic intrusion derived by partial melting of mantle cumulates. The high calcic plagioclase and low Mg/(Mg+Fe) mafic phases present in the FANs would not necessarily represent a primary feature of a crystallizing lunar magma ocean but instead would reflect partial melting processes occurring in the mantle (Longhi, 2003). The young ur-KREEP model age could, in principle, reflect late closure of the Sm-Nd and Lu-Hf systems due to tidal heating (Elkins-Tanton et al. 2011; McLeod et al., 2014) or internal heat production due to the decay of Th (Wieczorek and Phillips, 2000). Likewise, the young age of equilibrium of the mare basalt source region could result from slow cooling of the mantle associated with these processes, or from reheating after overturn caused by density instabilities inherited from primordial solidification of magma-ocean cumulates. In any case, isotopic equilibrium between ur-KREEP and the mare basalt source regions must be maintained until ~4.36 Ga in order to preserve their isotopic systematics.

The most significant difficulty associated with this scenario is placing it into the context of an earlier global-scale differentiation event. Specifically, mechanisms are needed that both preserve chemical and mineralogical differences inherited in mantle source regions from primordial magma ocean solidification, while maintaining isotopic equilibrium between these reservoirs for a significant period of time after magma ocean solidification. Another difficulty with this scenario is that it does not offer an explanation for the concordance between the 4.34-4.36 Ga ages of crustal samples with the ur-KREEP and mare basalt source model ages of 4.35-4.37 Ga other than coincidence. If this scenario is correct, further development of differentiation models for the Moon are likely to be required.

CONCLUSION

The Sm-Nd and Rb-Sr chronology of lunar highlands samples is obscured by metamorphism associated with the late heavy bombardment at ~3.8 Ga that has disturbed the isotopic systems used to define their ages. Interpretation of published ages is also made more difficult by the fact that, over the past 40 years, laboratories have measured different values for isotopic standards, and used different regression models to calculate ages. Isotopic data for highland rock samples published in the literature have been re-normalized to common standard values and are used to calculate comparable ages and initial isotopic compositions using IsoPlot 4.15. The reliability of these ages is evaluated using five criteria. These criteria include whether: (1) ages are confirmed by multiple chronometers, (2) there is limited scatter on isochron plots, (3) the chronometers used to define an age are resistant to disturbance by thermal metamorphism, (4) initial isotopic compositions agree with petrogenetic models developed for the origin of particular rock suites, and (5) abundances of Sm and Nd is mineral separates match those measured in situ by ion microprobe. This analysis demonstrates that the oldest ages are some of the least reliable and that the most reliable ages determined for lunar crustal rocks are generally less than 4.36 Ga. Ages between 4.35 and 4.37 Ga age are also recorded by model ages for formation of urKREEP, equilibrium model ages of the mare basalt source regions, a peak in lunar zircon ages, and in the oldest terrestrial zircon age. There are two scenarios that can account for the widespread occurrence of ages between 4.35 to 4.37 Ga on the Moon. In the first, this age range represents the closure of the various chronometers during primordial solidification and cooling of the magma ocean. This scenario is not consistent with the older Pb-Pb ages determined on some lunar zircon cores that are up to 41 Ma older than 4.37 Ga. An alternative scenario accounts for the

4.35 to 4.37 Ga ages observed in lunar crustal rocks as a result of a widespread pulse of magmatism occurring on the lunar nearside. This scenario does not provide a mechanism to explain the concordance of ages determined for ur-KREEP formation and mare basalt equilibrium with crustal ages recorded in the crustal rocks of the FAN and Mg-suites. If this scenario is correct, then petrogenetic models for the differentiation and evolution of the Moon must be further developed.

ACKNOWLEDGEMENTS

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-JRNL-. This work was supported by NASA Cosmochemistry grants NNH12AT84I to L.E.B and NNX10AI77G to C.K.S. We are grateful for reviews by Larry Nyquist, Qing-zhu Yin, and Alan Brandon.

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Figure Captions.

Figure 1. Summary of Sm-Nd ages determined on highlands rocks samples. This system is the most resistant to resetting by thermal metamorphism (Gaffney et al., 2011) so these ages are the most representative of chronology in the lunar highlands. Nevertheless, these data imply that ferroan anorthosite (FAN) and Mg-suite magmatism was contemporaneous for ~ 200 Ma. Shaded vertical area represents range of ur-KREEP and mare basalt model ages. Data from Alibert et al., (1994); Borg et al., (1999, 2011, 2013); Brandon et al. (2009); Boyet and Carlson (2007); Carlson and Lugmair (1979, 1981a; 1981b; 1988); Carlson et al. (2013); Edmunson et al. (2007; 2009); Lugmair et al. (1976); Nakamura et al. (1976), Norman et al., (2003); Nyquist and Shih (1992); Nyquist et al. (1981, 1995, 2006); Rankenburg et al. (2006); Shih et al. (1993); Snyder et al. (1995).

Figure 2. Plot of isochron ages determined for highlands rock samples versus reliability index of age determination demonstrating that the oldest ages are some of the least reliable. Data and references from Table 1.

Figure 3. Age versus initial Nd isotopic composition determined from Sm-Nd isochrons of highlands rock samples. The ur-KREEP Sm-Nd model age of 4389±45 Ma is defined by the intersection of a line regressed through age data with a chondritic growth curve. All age data with reliability indices ≥4/5 that have not been superseded by ages with higher reliability indices are used in the regression with the exception of sample 67667. The chondritic growth curve is calculated assuming $^{147}Sm/^{144}Nd$ = 0.1967 and $^{143}Nd/^{144}Nd$ = 0.512638 (Jacobsen and Wasserburg, 1980).

Figure 4. Histogram of zircon spot ages determined by ion microprobe. Ages are divided into 10 Ma bins. Note peak in ages at 4335 Ma. Oldest ages are overrepresented on this diagram due to numerous (41) analyses of a single zircon from breccia 72215 spanning an age range of 88 Ma. Data from Grange et al., (2009; 2011), Meyer et al. (1996), Nemchin et al. (2006; 2008; 2009a; 2009b), Pidgeon et al., (2007), and Taylor et al. (2009).

Figure 5. Histogram of zircon spot ages with 1 sigma uncertainties demonstrating sharp termination of zircon ages at ~4.4 Ga. Data sources same as Figure 4.

Figure 6. Histogram of oldest lunar zircon ages compared to the peak of lunar zircon ages, model ages for ur-KREEP, model age for the mare basalt source region, and FAN 60025.

Figure 7. Histogram of all ages discussed in the text. Panel A includes all igneous crystallization ages colored according to reliability index. Labeled samples have been analyzed multiple times. Panel B are ~400 zircon Pb-Pb spot ages determined by ion microprobe. Black fill represent spots from single zircon in breccias 72215 analyzed 41 times. Panel C includes model ages for ur-KREEP from the literature,

and model ages published for the mare basalt source region. Dark gray field is average mare basalt source model age and light gray field represent average ur-KREEP model ages calculated here. Thick dashed line is represents the age for the oldest terrestrial zircon 01JH36-69. Data sources are listed in Figure captions 1 and 3 and Table 1 and also include Valley et al. (2014).